UTILIZATION OF ATOMIC ABSORPTION SPECTROPHOTOMETRY FOR THE STUDY OF ADSORPTION KINETICS IN THE LIQUID PHASE

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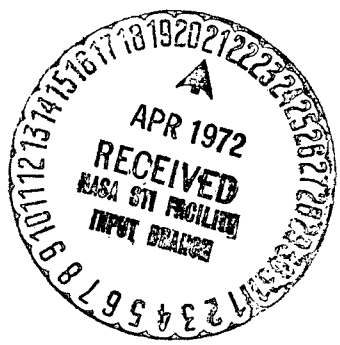

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UTILIZATION OF ATOMIC ABSORPTION SPECTROPHOTOMETRY FOR THE STUDY OF ADSORPTION KINETICS IN THE LIQUID PHASE

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Bernard Buathier and Roger Neybon*

ABSTRACT. Atomic absorption spectrophotometry is a preferred analysis instrument for the continuous measurement of concentration variations of a cation in solution. There is one important application, which is the study of adsorption kinetics in the liquid phase of platinum with respect to adsorbants such as coal or alumina. An instrument which couples the reactor to the spectrophotometer is described. The response time of this unit is on the order of one second. Thus, if it is difficult to determine the rapid adsorption kinetics such as that of platinum with respect to coal, it is very convenient to study a slow adsorption kinetic process such as that of alumina. It is easy to obtain the adsorption velocity at the origin of time using a continuous measurement technique. It is also possible to determine the adsorption limit using discontinuous measurements, which have the advantage of consuming only a very few cations.

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I. INTRODUCTION

As Slavin [1] recently pointed out, it was only ten years ago that Walsh [2] introduced a method of analysis called atomic absorption spectrophotometry. For the last few years there has been a particularly rapid

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**Numbers in the margin indicate pagination in the original foreign text.

development of this method and this is undoubtedly not only due to the inherent advantages of the method, but also due to the continuing work in attempting to resolve the various problems associated with the use of this technique.

Some of the specific properties of atomic absorption spectrophotometry are the very small effect of disturbances and a very high sensitivity. As Slavin [1] indicated, the possibilities of atomic absorption are far from being implemented at the present time, and a number of problems have yet to be solved.

In this study we will attempt to determine the possibilities of atomic absorption spectrophotometry in the continuous analysis of a cation solution, the concentration of which is varied. This analysis problem occurred frequently and especially in the study of salt dissolving processes, metal corrosion in the liquid phase and in the adsorption process of a cation by an adsorbant. We do not intend to present an example for each of these three cases and propose to only give an example for the latter case. Thus we attempted to carry out a continuous measurement of the adsorption kinetics of the platinum cation by an adsorbant such as activated charcoal or activated alumina. However, this method will certainly be valid for all the other cases because of the specific features of atomic absorption spectrophotometry. The other limitation will be connected with the response time of the apparatus.

II. DESCRIPTION OF THE APPARATUS

The apparatus is sketched in Figure 1 and consists of two essential parts. These are the atomic absorption spectrophotometer and the reactor which has circuits for continuous analysis.

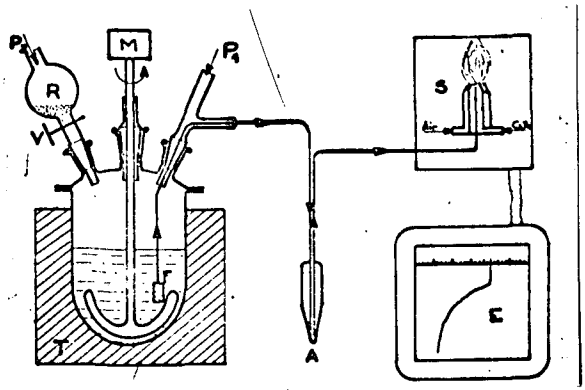

Figure 1. Description of the instrument:

M - motor; R - adsorbant reservoir; V - input valve; F - filter; T - thermostat; A - buffer volume; S - spectrophotometer; P_1 - filtration pressure; P_2 - injection pressure.

1. Atomic Absorption Spectrophotometer

The atomic absorption instrument consists of:

— a Westinghouse cathode crucible source fed with direct current and coupled to a 400 Hertz modulator;

— a Perkin-Elmer vaporizer with burner head for a $N_2O + C_2H_2$ flame (S, Figure 1);

— a Beckman DU monochromator with a IP 28 detector.

— an amplifier connected with the modulator. The signal is transmitted to a Meci (Leeds and Northrups) E. recorder.

Platinum was analyzed at the resonance line λ = 2,659 Å. The width of the input slit of the monochromator is equal to 0.1 mm, which corresponds to a spectral width of 2 Å.

The supply current of the crucible cathode is 20 mA

The supply voltage of the detector is 500 V

The amplification gain is 800

The gas yields are determined such that the flame is slightly oxidizing /2195
(minimum height of the rose-colored cone) and the pressures are equal to:

C_2H_2 . . . . . 0.5 bar

N_2O (vaporization and auxiliary) . . . . . 2 bars

These conditions makes it possible to considerably reduce the interferences due to the alumina, because the presence of 20 ppm of aluminum does not modify the measurements of the platinum concentration.

2. Reactor and Continuous Analysis System

The classical pyrex reactor (Figure 1) is covered with a cover having three tubes. The central tube is for rotating the agitator M. The second tube makes it possible to rapidly introduce the adsorbant (in 1 to 2 seconds) in a continuous way into the reservoir R using the valve V. This substance is introduced more rapidly by using a gas under a pressure P_2 equal to 1.5 bar. Continuous flow of the liquid is provided in the third tube which is inside a plastic tube having an inner diameter of 0.8 mm, which is under the pressure P_2 equal to 1.2 bar. There is a filter F (detail, Figure 2) at the end of this tube.

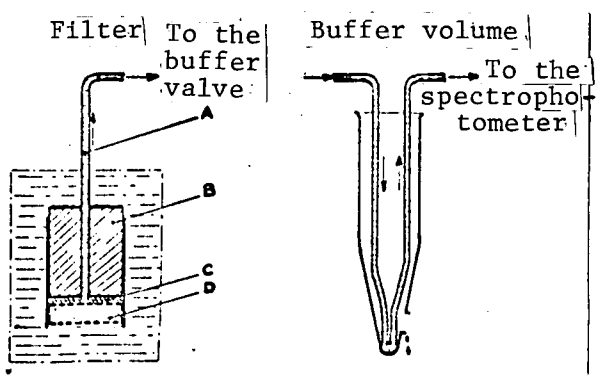

Figure 2. Detail of the filter and the plug volume:

A - polythene tube; B - PVC cork;
C - cotton plug (thickness 1 mm);
D - No. 2 calcinated glass pellet.

The aspiration yield of the solution by the spectrophotometer is equal to 5 cm^3 per minute. The yield of the liquid extracted from the reservoir is maintained equal to this value by means of the pressure P_1. The small fluctuations are equalized by means of the buffer volume A (detail, Figure 2). The liquid volume contained in this reservoir A is reduced to a minimum value by the operator and it is much lower than 0.2 cm^3. The liquid volumes contained in the filter F and in the plastic material tube are equal to 0.1 and 0.14 cm^3 respectively.

The filter F consists (detail, Figure 2) of a calcinated glass pellet No. 2 (D) with a cotton plug (C), the thickness of which is approximately 1 mm. This cotton plug, as well as the polyethylene tube (A) used to transport the solution to the spectrophotometer, are kept in the filter by means of the PVC cork B.

The volume of the plastic tube brings about a spectrophotometer analysis delay equal to about 2 seconds. Thus, when the platinum concentration of the solution located in the reactor varies very rapidly from 1 to 0 g per liter, this variation is recorded with a delay. In addition, there is certainly a longitudinal diffusion phenomenon along the tube. There is also another diffusion phenomenon which is even more important in the filter and in the buffer volume A. The measured concentration appears somewhat different than the true variation. Thus, in Figure 3, we show the recording of the variation in the platinum concentration obtained after 1/5 seconds. It can be seen that the measured variation is on the order of 1 second, and therefore there is a considerable inertia of the apparatus.

III. EXPERIMENTAL RESULTS AND CONCLUSIONS

The curve for the platinum solution concentration variation is obtained directly as a function of time. In order to not change the amount of platinum contained in the reactor too much, it is probably interesting to carry out the analysis in a discontinuous manner (Figure 4). This can be done rapidly by making the pressure P_1 equal to 0 and then equal to 1.2 bars.

1. Adsorption Kinetics of Platinum on Activated Charcoal

The activated charcoal utilized is L 2 S (CECA) acticarbon with the following essential characteristics:

- granularity between 5 and 75 microns, average value 40 microns;
- total area: (BET nitrogen) 1,100 m^2/g;

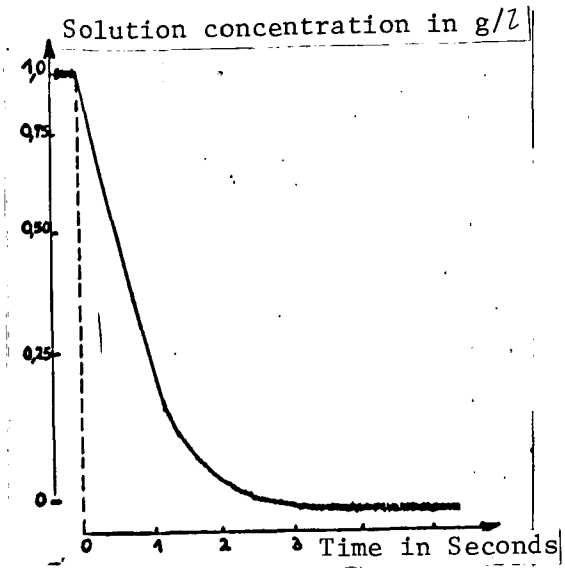

Figure 3. Response time of the apparatus.

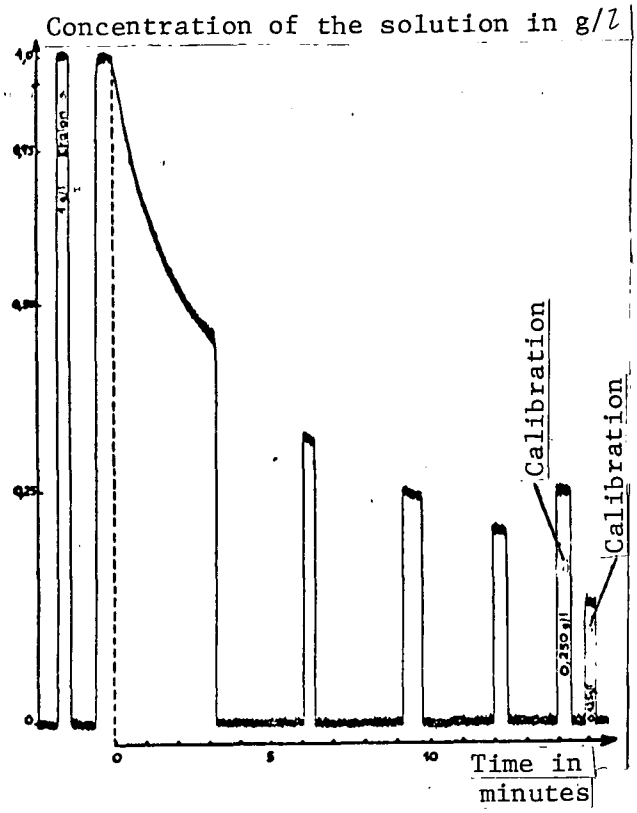

Figure 4. Experimental curve of the adsorption kinetics of platinum with respect to alumina using calibrations at the beginning and at the end of the experiment

— total porosity: 0.68 m^3/g.

In each case, 5 grams of L 2 S activated charcoal was used and 200 cm^3 of hexachloroplatinic acid solution were used.

Figure 5 shows the two curves obtained for a different value of the platinum concentration. Curve I corresponds to a concentration of 0.5 grams of platinum per liter of solution. Curve II corresponds to a concentration of 1 gram of platinum per liter. One can therefore see that the adsorption is almost complete at the end of 30 seconds and one half of the platinum is adsorbed during the first 8 seconds. However, the response time obtained by the method we are recommending is about 1 second (Figure 3). Therefore one can understand why the study of the rapid adsorption kinetics such as that of platinum by charcoal is more delicate, even though it is more convenient.

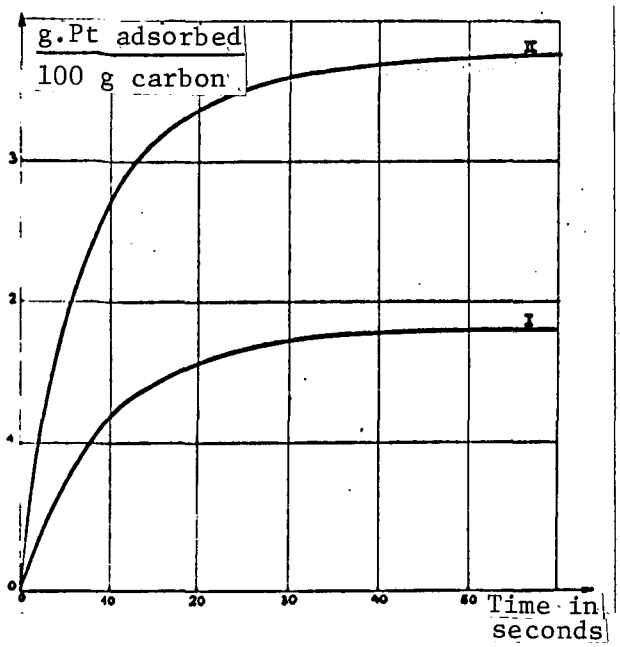

Figure 5. Adsorption kinetics of platinum with respect to activated charcoal in powder — 5 g acti-carbon L 2 S (CECA):

I. Hexachloroplatinic acid solution with 0.5 g/ℓ of platinum;

II. Hexachloroplatinic acid solution with 1 g/ℓ of platinum.

2. Adsorption Kinetics of Platinum on Activated Alumina

The adsorbant is activated alumina A in "semolina" form (Péchiney-St Gobain). It has the following main characteristics:

— granularity: sifted in a 160 to 200 micron screen;

— total area: (BET nitrogen) 260 cm^2/g;

— total porosity: 0.42 cm^3/g.

The weight of the alumina A is equal to 5 grams and the hexa - chloroplatinic acid solution volume is 200 cm^3. Optimum agitation is performed by the agitator.

Figure 6 shows the curves for the adsorption kinetics of platinum. Curve 1 corresponds to a concentration of 0.5 grams of platinum per liter and curve 2 corresponds to a concentration of 1 gram per liter. It can be seen that the adsorption rate is considerably slower when the adsorbant is alumina and that the response time of the apparatus then becomes negligible.

3. Conclusions

Even though it seems that the method which we are recommending is a delicate one for studying rapid adsorption kinetics such as that of platinum

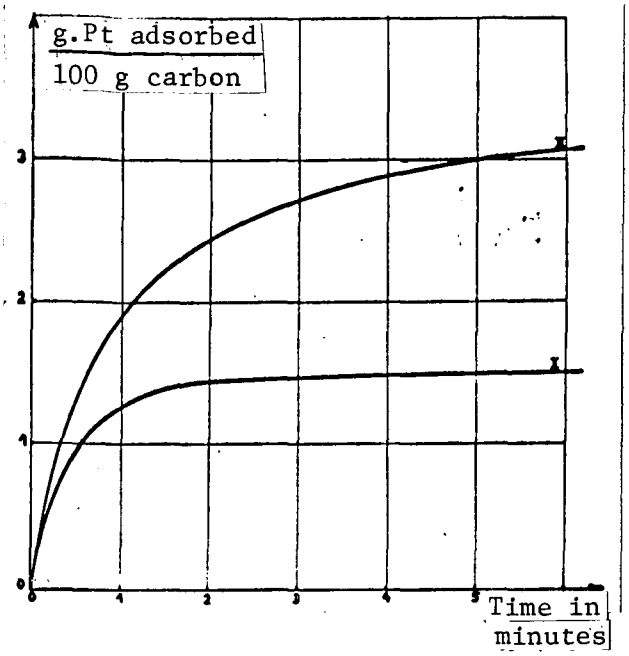

Figure 6. Adsorption kinetics of platinum on alumina — 5 g alumina A, 160 - 200 microns:

I. Hexachloroplatinic acid solution with 0.5 g/ℓ platinum;

II. Hexachloroplatinic acid solution with 1 g/ℓ of platinum.

on activated charcoal, one must nevertheless acknowledge that it is very convenient and sufficiently accurate when the adsorption kinetics are sufficiently slow. Thus it is possible to determine the adsorption rate at the initial time and to also refine the value of the adsorption limit. Finally, by plotting curves according to the model given in Figure 4, the amount of platinum consumed in the analysis becomes negligible. The emission spectrophotometry can be also used, but atomic absorption spectrophotometry has the advantage of reduced sensitivity to disturbances.

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